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Oxidation resistant aluminized MCrAlY coating prepared by Sparks Plasma Sintering (SPS)

By D. Oquab, C. Estournes and D. Monceau

Abstract:

MCrAlY coatings for high temperature applications have been widely studied in the last two decades. They are usually fabricated by plasma spraying or electrolytic techniques. The present work concerns NiCoCrAlYTa single and multi layered coatings on an AM3® nickel base superalloy in order to explore new potentiality of Sparks Plasma Sintering (SPS) technique. The first results reported in this paper are promising and open the way to faster development of new coatings with complex structure and composition.

Keywords: MCrAlY, high temperature coatings, SPS, multilayer coatings.

Introduction

Nickel base superalloys are well known for their excellent mechanical properties in high temperature applications such as aeronautic and energy production gas turbines. But due to their lack of oxidation and corrosion resistances, these materials are protected by nickel aluminides or MCrAlY (where M= Co, Ni or Co/Ni) coatings. NiCoCrAlYTa presents very good corrosion resistance and is used as a standalone coating or as a bond-coat in thermal barrier coating systems *[1, 2]*. The usual ways of coatings preparation are Physical Vapour Deposition (PVD), Low Pressure (LPPS), Vacuum (VPS) *[3]* or Air Plasma Spraying (APS), High Velocity Oxy Fuel (HVOF) spraying *[2, 4]*, and finally electrolytic deposition methods are also used *[5]*.

Works on multilayered or compositional gradient coatings *[1]* have been presented in order to combine the better oxidation resistance of an aluminized external layer with the hot corrosion resistance of NiCoCrAlYTa and the good compatibility of NiCoCrAlYTa with the Ni base superalloy (less interdiffusion than between a nickel aluminide coating and a superalloy). On the other hand, composite and multilayered materials preparation have been reported by Mukrami et al *[6]* using a Spark Plasma Sintering technique.

In the present work, we explore some new potentialities of Sparks Plasma Sintering (SPS) technique, to prepare NiCoCrAlYTa single and multi layered coatings on a nickel base superalloy substrate. The first results presented here are very promising and open the way to faster development of new coatings. Particularly, this technique allows developing coatings with complex structure, e.g. multilayered deposits or coatings with compositional gradient, over-aluminized layers at the surface or at the interface. SPS offers the possibility of building easily, compared to other methods *[7, 8]*, new formulations or new structural architectures. The objective of these new architectures or modified coatings is to improve high temperature corrosion and oxidation behaviors of those materials by combining properties of different compositional layers.

Experimental procedures

The sample has been sintered using Spark Plasma Sintering apparatus (Model Dr Sinter SPS-2080 SPS Syntex INC Japan). The SPS equipment consists of a pulsed (3.3 ms of duration) direct current generator, an hydraulic press system, a vacuum and water cooled chamber, upper and lower punch electrodes graphite spacers, punches and sintering die and finally control systems for the temperature (thermocouple or optical pyrometer), environment pressure inside the chamber and for the positioning of the lower electrode on z-axis which allows to follow the shrinkage of the sample. The preparation chamber is presented on Figure 1.

The substrate used for this study was a 8mm diameter disc prepared from a single crystal nickel-base superalloy AM3® rod, whose composition is given in table 1. The substrate has a 1 mm diameter hole going through the 1 mm thick sample (Fig. 2). Before use, the substrate surface was mechanically polished up to 0.25 µm diamond grit.

Two different architectures have been fabricated using sintering in the SPS machine. For the first sample, the NiCoCrAlYTa powder (0.62 g without any sintering aids) has been loaded on each side of an AM3 single crystal substrate in a cylindrical die with an inner diameter of 8 mm (Fig.2). The pulse sequence used is 12-2 (pulses - dead time or zero current) as recommended by the SPS equipment constructor. The temperature was monitored and regulated using a thermocouple fixed in a little hole situated at the surface of the die. The temperature was automatically raised from room temperature at 1000 °C with a heating rate of 100 °C/min. An uniaxial pressure of 50 MPa was applied in the first 2 min of the cycle until the end of the temperature step (3 min) at 1000 °C. In these conditions, during the sintering cycle, the voltage reached a maximum value of 4.3 V and the maximum value of current passing through the die reached the value of applied 470 A.

For the second sample, similar architecture have been prepared with same conditions except that aluminium cylindrical sheets (8 mm diameter, 10 µm thick) have been intercalated on one side between the NiCoCrAlYTa powder and the AM3 substrate, and on the other side between the protecting graphite foil and the NiCoCrAlYTa powder (Fig.3). Other parameters remained unchanged.

After sintering, the graphite foil from the sample surface was eliminated by oxidation of carbon during a 10 min heat treatment at 800°C under air. The sample was mechanically cleaned in order

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to eliminate surface particles.

X-Ray diffraction, using a Seiffert system with a low incidence angle of 5°, was carried on mechanically cleaned and slightly polished sample surface, in order to remove remaining surface graphite or particles. For SEM and EDX analysis a LEO 435VP microscope and an IMIX-PC was used. Samples were cut to examine the cross section by SEM. The cross sectioned surface preparation consisted of mechanical polishing up to 4000 grit SiC polishing paper, and cleaning ultrasonically before rinsing with acetone and alcohol. Samples were analyzed by SEM and EDS techniques.

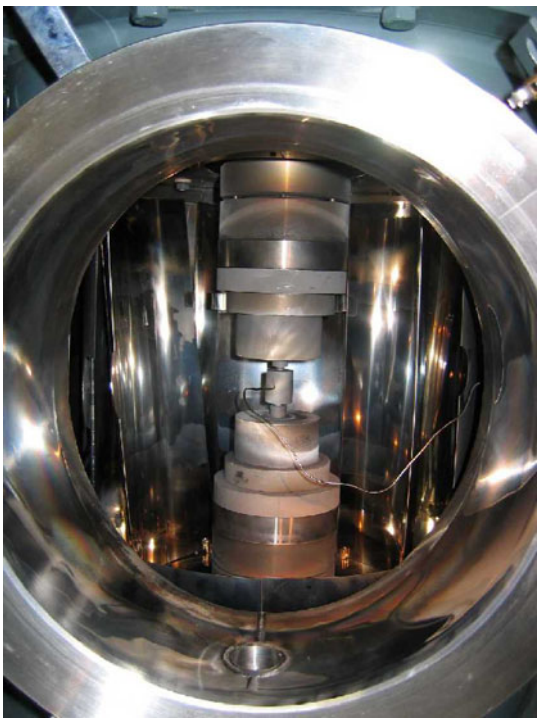

Figure 1: Sample preparation chamber of the Spark Plasma Sintering (SPS) apparatus, Model Dr Sinter SPS-2080 SPS Syntex INC Japan.

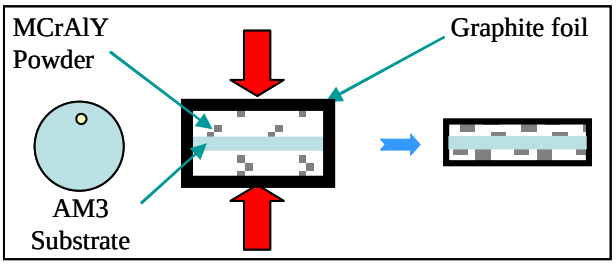

Figure 2: Sample preparation method for the MCrAlY coating

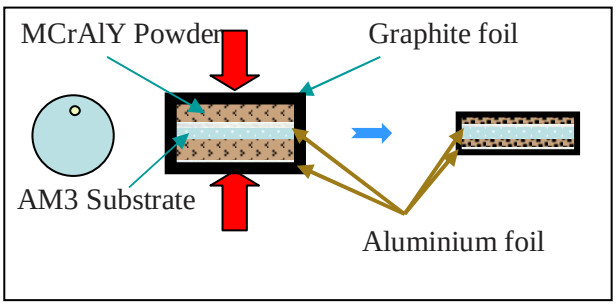

Figure 3: Sample preparation method for MCrAlY coating with Al sheets inserted in the preparation.

Table 1. Composition (wt%) of AM3 substrate and NiCoCrAlYTa powder

Alloy	Ni	Co	Cr	Al	Ta	Mo	Ti	W	Y
AM3	Bal	5.2	7.8	5.0	5.8	2.1	1.5	8.0	-
MCrAlY	Bal	23	20	8	4				0.6

Results and discussion

SPS prepared NiCoCrAlYTa coating shows a very homogenous microstructure with no porosity, and very good adherence in any part of the AM3 substrate including inside the substrate hole, as shown by cross sectioned sample observations presented in Figure 4. (Please note that in the following, we will use the term of coating for the layer issued from MCrAlY powder sintering, even if its thickness is very important).

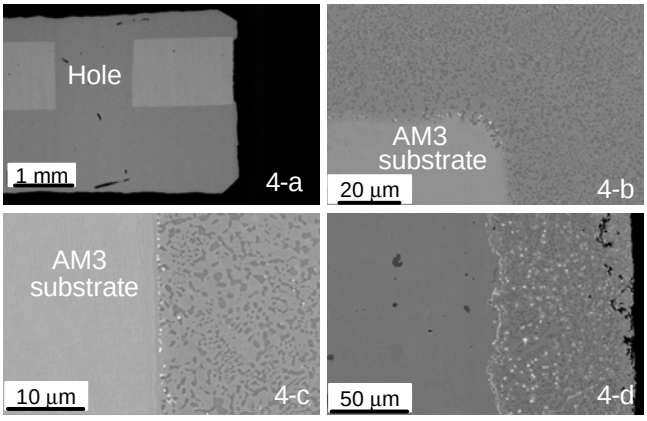

Figure 4. SEM observations of a cross section of as prepared NiCoCrAlYTa coating on AM3 single crystal substrate showing the perfect adhesion of the coating in a complex geometry substrate: a) overall view, b) hole region, c) detail of the interface, d) vacuum plasma sprayed MCrAlY for comparison with SPS coating

The NiCoCrAlYTa coating is composed of three major phases, gamma (FCC Ni), gamma prime (Ni_3Al) and beta (NiAl). The interface between AM3 superalloy and NiCoCrAlYTa coating shows an interdiffusion layer of about 2 µm thick, and segregation of tantalum carbide TaC phase was observed at the outer side of the diffusion layer. For comparison, a SEM-BE image of an industrial NiCoCrAlYTa coating prepared by vacuum plasma spraying (VPS) is presented in Figure 4-d. The same phases are present in SPS and VPS coatings, but VPS shows a rougher substrate/coating interface and some porosity in the external part.

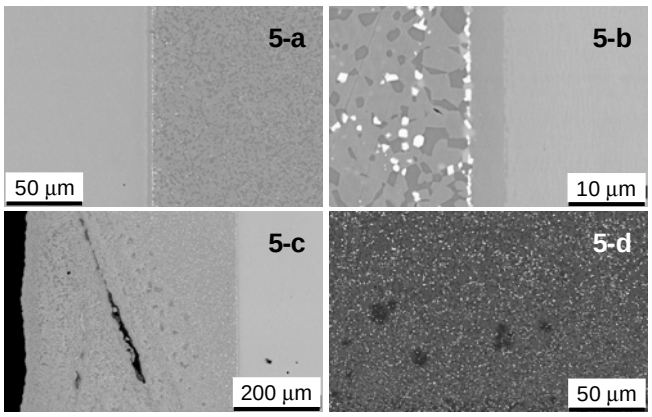

Figure 5. NiCoCrAlYTa coating prepared by SPS after 6 h heat treatment at 1063°C. (a,b) 2 µm thick interdiffusion layer, (c) carbides close to a flake of graphite foil remaining form SPS process, (d) carbides developed under the NiCoCrAlYTa surface.

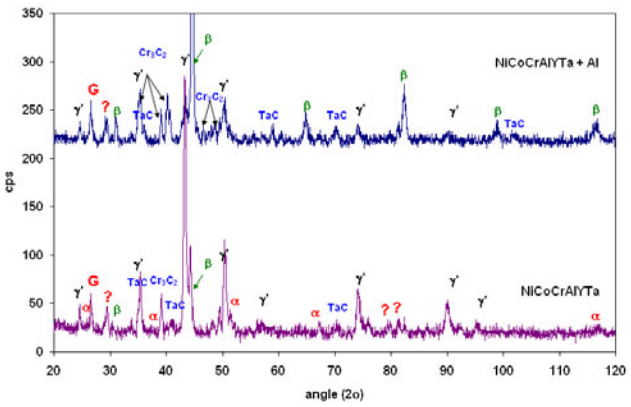

Figure 6. θ-2θ XRD pattern with 5° low incidence angle. (top) aluminized NiCoCrAlYTa side, (bottom) NiCoCrAlYTa without aluminization (G stands for graphite, α for α-Al_2O_3)

A second sample was prepared to show the feasibility of coatings with a gradient of composition. A 10µm thick aluminium foil was intercalated between AM3 substrate and NiCoCrAlYTa powder on one side of the sample, and in the other side, the aluminium foil was placed between the powder and the mounting graphite foil (Fig. 3).

A 6 h heat treatment at 1063 °C was applied to the previously described sample, in order to reproduce the industrial homogenization heat treatment of the superalloy. The resulting microstructure shown on Figure 5, indicates no major change in the coating structure or in the interdiffusion layer. On both un-annealed and annealed samples, some chromium carbides phases were detected under the NiCoCrAlYTa surface (Fig. 5d) or near the region with a graphite foil flake remaining from the SPS process (Fig. 5c). This is an important observation because these carbides could have a detrimental effect on the high temperature oxidation behaviour.

Both surfaces of the sample, with and without aluminium at the surface, were analyzed by XRD with a low angle incidence (Fig. 6). At the surface without aluminium foil, gamma prime Ni_3Al phase is the major constituent and beta NiAl phase is detected. Some tantalum carbide TaC, chromium carbide Cr_3C_2 and graphite from remaining graphite foil are also identified. At the Al rich surface, the major detected phase is beta-NiAl, but gamma prime Ni_3Al is also present. TaC and Cr_2C_3 are more obvious than at the un-aluminized surface. SEM observations of the cross-sectioned sample (Fig. 7) confirm higher concentration of chromium carbide in a thin subsurface layer (about 10 µm) in the case of aluminized surface (Fig. 7-b), whereas carbides are dispersed in a larger depth (about 100 µm) in the case of un-aluminized surface (Fig. 7-c).

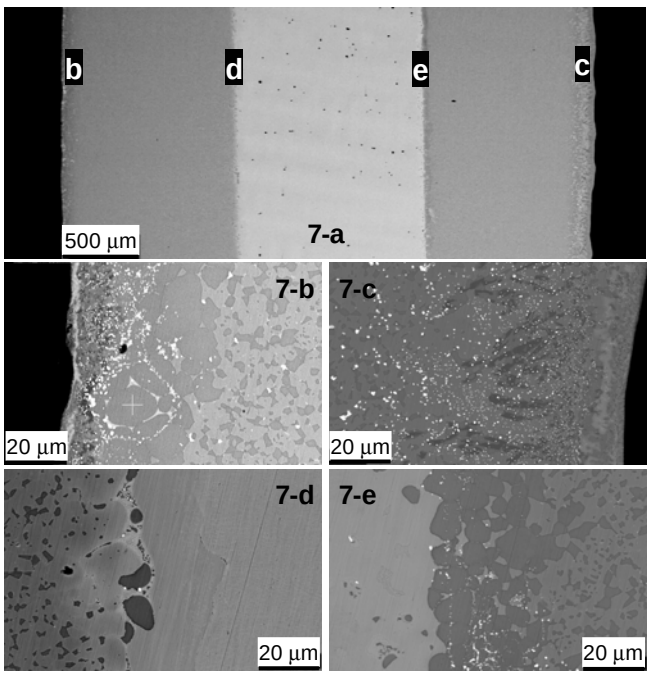

Figure 7. SEM backscattered electron images of NiCoCrAlYTa coatings on AM3: (a) Global view of the sample cross-section, from let to right: Al rich layer, NiCoCrAlYTa layer, AM3 substrate, Al rich layer at the interface, NiCoCrAlYTa and carbide phase formed near the coating surface. Frames indicate areas for which details are presented below. (b) Detail of outer Al rich layer, (c) Detail of carbides formed under the NiCoCrAlYTa surface of the un-aluminized face, (d) Coating/substrate interface without Al rich layer, (e) Coating/substrate interface with Al rich layer.

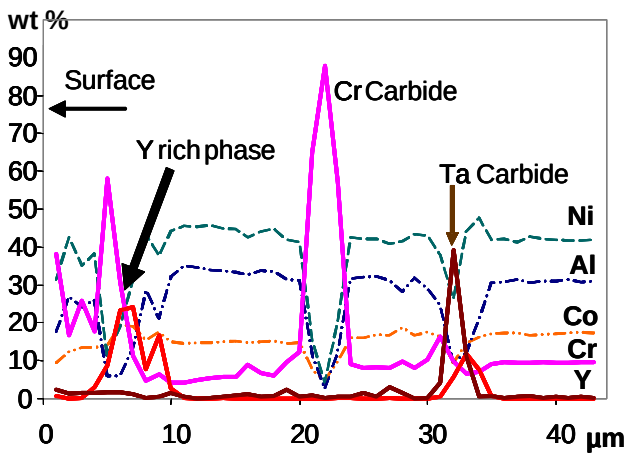

Figure 8. EDS quantitative line profiles of the un-aluminized surface cross-section indicating very high content of yttrium (>20wt%) in the Y-rich phase. (Note that the average Yttrium content in the MCrAlY powder is only 0.6wt%).

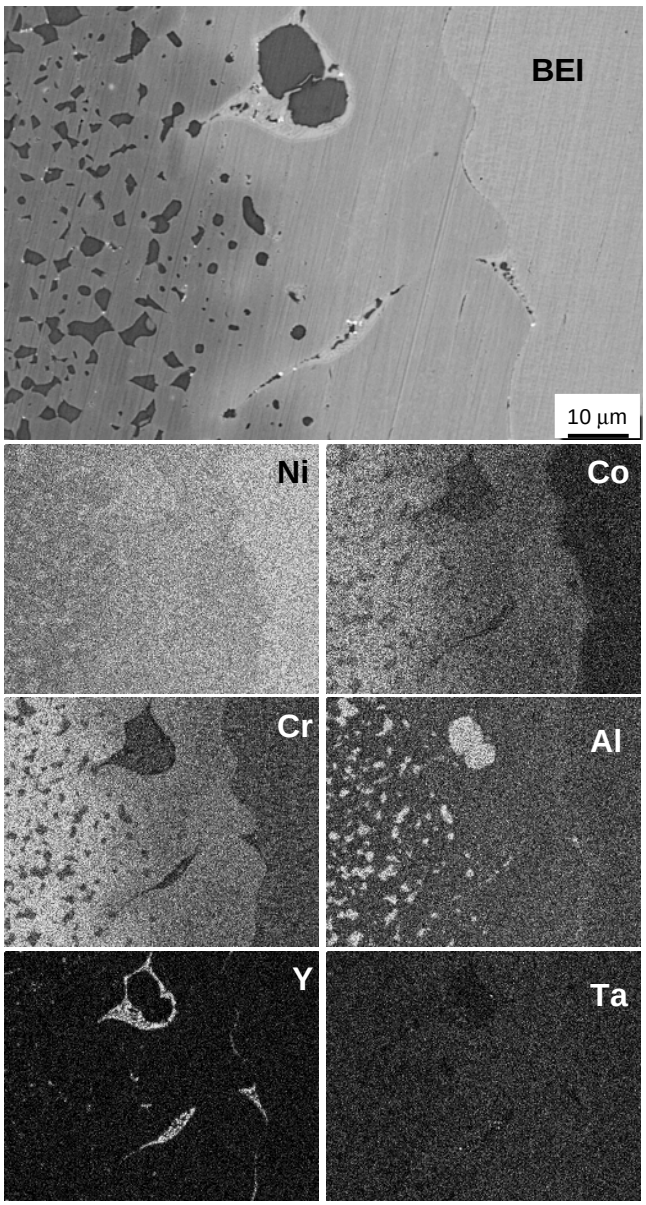

Figure 9. BSE image and X-ray maps of the substrate-NiCoCrAlYTa interface region showing the formation of an interdiffusion zone of about 40µm thick and some Y-rich precipitates.

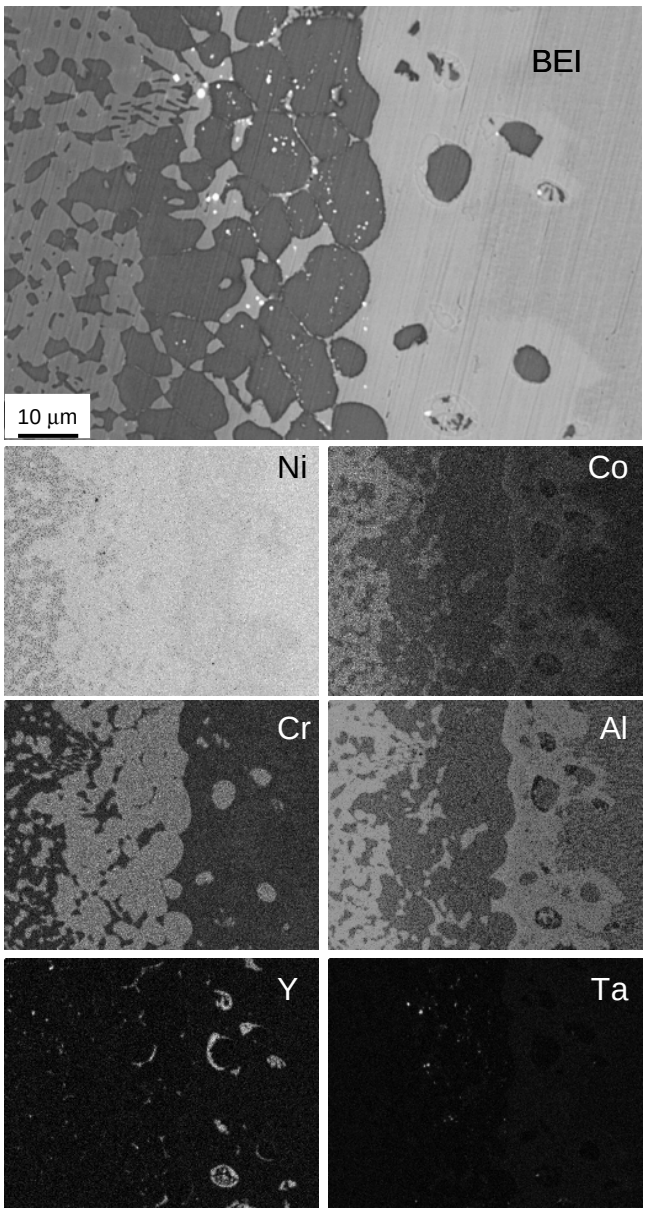

Figure 10. BSE image and X-ray maps of the substrate-NiCoCrAlYTa aluminium rich interface region showing the formation of beta-NiAl over the interdiffusion gamma layer. Some Y-rich precipitates are present in the gamma layer.

Addition of aluminium foil leads to a compact, more or less continuous beta phase formation, both at the NiCoCrAlYTa surface and at the substrate/coating interface (Figs. 7-b and 7-e). When located at the surface, only a thin layer containing chromium carbide and a Y-rich phase are observed at the outer region. EDS analysis shows that the Y-rich phase contains up to 23 wt% of Yttrium as shown in EDS quantitative line profile presented on Figure 8, whereas the Y concentration in the original NiCoCrAlYTa powder is about 0.6 wt% only. On the XRD diagram, one diffraction peak remained unidentified could be due to this phase. We observed previously than the aluminization at the surface of the NiCoCrAlYTa reduces the depth of the carburized zone, and we also note that it reduces also the amount of the Y-rich phase. Al-rich beta phase seems to play as a diffusion barrier for carbon, when present at the surface.

X-ray maps corresponding to the substrate-MCrAlY interface (Figure 9) and aluminium enriched substrate-MCrAlY interface (Figure 10) show very “clean” interfaces with about 40µm thick interdiffusion layers. Aluminium enrichment leads to beta NiAl formation at the interface.

Conclusions

This study demonstrates wide possibilities of preparing high temperature bulk, single layered and multilayered coatings by Sparks Plasma Sintering method. The first results are very encouraging because the prepared coatings and layers present homogenous structures with good adherence and an uniform inter-diffusion layer between the single crystal substrate and the coating. No porosities are observed, even in the case of the filling of a 1 mm diameter and 1 mm deep hole. Because of the high carbon activity due to the graphite die, chromium carbides Cr_3C_2 and some TaC are formed up to 100 µm deep subsurface layer. When the surface of the coating is covered with a 10 µm thick

aluminium foil, a beta-rich external aluminized zone is formed with a much lower amount of carbides. This aluminization is easy to process and leads to a beta-phase rich external coating with a excellent high temperature oxidation potential, and an internal gamma/gamma prime/beta NiCoCrAlYTa coating with a known excellent high temperature corrosion resistance and limited interdiffusion with the nickel base single crystal substrate. Moreover, the application of an aluminium foil at the coating/substrate interface shows that this technique can be used for an easy local aluminization of complex coating systems, without porosity despite of the low melting point of aluminium.

Acknowledgments:

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